

Nano-Mechano-Electrochemical Aspect of Passive Metal Surfaces

Masahiro Seo and Makoto Chiba

Graduate School of Engineering, Hokkaido University
Kita-13 Jo, Nishi-8 Chome, Kita-ku, Sapporo 060-8628,
Japan

Passive metal surfaces are covered with very thin oxide films, i.e., passive films which sustain the corrosion resistivities of metals. If the passive films with a thickness of nano-meters are locally broken down and not repaired, the metals are subjected to localized corrosion. The mechanical and electrochemical properties of passive metal surfaces are closely correlated to the local breakdown of passive films. However, there have been few studies on correlation between mechanical and electrochemical properties of passive metal surfaces. It is well known that the corrosion resistivities of passive metals are increased with a chromate or dichromate treatment. In this study, in-situ nanoindentation combined with AFM was performed on the passive single crystal iron surfaces to investigate the improvement of corrosion resistivities due to a dichromate treatment from the nano-mechano-electrochemical viewpoint.

Single crystal iron (100) and (110) disc-shaped plates with a diameter of 10 mm and a thickness of 1.0 or 1.4 mm were used in this experiment. The iron specimens were mechanically polished with alumina abrasives and then finally electropolished with a constant current density of 32 mA cm⁻² in a mixture of 70 % HClO₄ and glacial CH₃COOH (1:20) at 17 °C. The electrolyte solution employed was pH 8.4 borate solution. The nanoindentation apparatus (Hysitron Co.) was attached to the AFM (Digital Instruments, Nanoscope IIIa) in which the electrochemical cell was set. The nanoindentation tests were performed on the iron surfaces using a Berkovich pyramidal diamond indenter. The Berkovich diamond indenter was attached to a tungsten rod for use in liquid. The iron specimens were cathodically reduced with a constant current density of 30 μA cm⁻² in pH 8.4 borate solution to remove the air-formed film. After the cathodic reduction, the specimens were passivated at 0.25 V (SHE) for 1 h in the renewed solution. For dichromate treatment, the iron specimens electropolished were immersed in 5 x 10⁻² M K₂Cr₂O₇ solution for 24 h and then passivated at 0.25 V (SHE) for 1 h in pH 8.4 borate solution. The in-situ nanoindentation tests of the passivated iron surfaces with and without dichromate treatment were performed under a maximum load, L_{\max} , of 100 μN - 500 μN and an indentation time of 10 s to measure the load-depth curves from which the mechanical properties of the passive surfaces were evaluated.

Figure 1 shows the effect of dichromate treatment on load-depth curves for the iron (100) surface passivated at 0.25 V (SHE) for 1 h in pH 8.4 borate solution. It is seen that the dichromate treatment tends to shift slightly the load-depth curves to the higher load and less depth. The similar effect was also observed for the passivated iron (110) surface. The hardness values of the iron (100) surface evaluated from the load-depth curves were plotted versus maximum load, L_{\max} , in Fig. 2. The detailed procedures for evaluation of hardness from load-depth curve were described elsewhere [1,2]. It is seen from Fig. 2 that the hardness of the passivated iron (100) surface is increased apparently with dichromate treatment except for

low maximum load, $L_{\max} = 100 \mu\text{N}$. Although the increase in hardness of the passivated iron (110) surface due to dichromate treatment was also observed, the effect was less than that of the passivated iron (100) surface because the hardness of the substrate iron (110) surface was higher by about 10 % than that of the substrate iron (100) surface [2]. In this experiment, the indentation depth was much larger than the thickness of passive film. Therefore, the passive film at outer edges of the indenter would be ruptured and repaired repeatedly during the indentation. The apparent increases in hardness of the passivated iron surfaces due to dichromate treatment may result from the promotion of repassivation brought with a chromium-enriched film.

References

1. M. Seo, M. Chiba and K. Suzuki, J. Electroanal. Chem., **473**, 49 (1999).
2. M. Seo and M. Chiba, Electorchim. Acta., accepted.

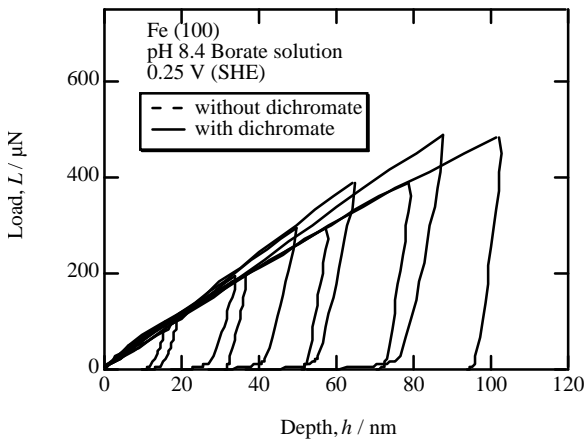


Fig. 1 Effect of dichromate treatment on load - depth curve for the iron (100) surface. The iron (100) surface was passivated at 0.25 V (SHE) for 1 h in pH 8.4 borate solution after immersion in 5 x 10⁻² M K₂Cr₂O₇ solution for 24 h.

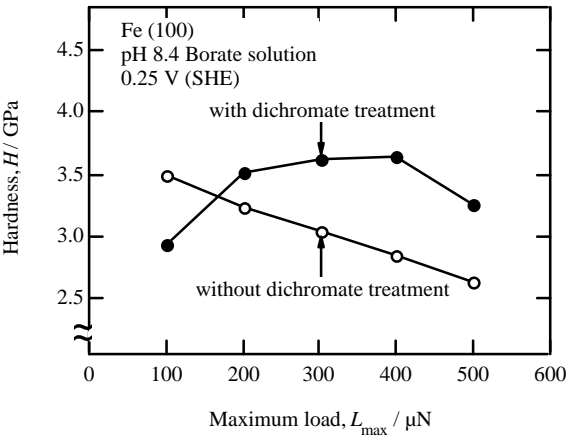


Fig. 2 Relation between hardness, H , and maximum load, L_{\max} , for the passivated iron (100) surfaces with and without dichromate treatment.